Three-Body Collision Contributions to Atomic Recombination and Collision-Induced Dissociation

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Recombination and collision-induced dissociation are among the most fundamental types of chemical reactions and are of great importance in all gas phase chemistry. Most of the energy that drives the world economy comes from the combustion of hydrocarbons (gasoline, coal, natural gas, etc.), and about half of the 196 reactions identified as important in combustion chemistry are recombination or collision-induced dissociation reactions. The overall chemical equation for any recombination reaction is the forward direction of

$$A + B + M \leftrightarrow AB + M,$$

where A and B are any atoms, molecules or radicals for which AB has bound states, and the third-body M is any species that can carry away the excess energy. The reverse direction of this reaction is collision-induced dissociation.

In the first half of this century, although they could not do accurate calculations, writers allowed for the possibility that recombination might occur in a single collision, i.e.,

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by a true three-body collision. However, for the past 30 years, nearly all authors have assumed that, in the case in which the third-body M is relatively inert, the reaction proceeds only via the Lindemann energy transfer mechanism,

$$A + B \leftrightarrow AB^*,$$
$$AB^* + M \leftrightarrow AB + M.$$

Here the species with an asterisk, AB*, represents metastable or quasibound intermediates. Note that this mechanism is a sequence of two-body collisions.

In cases where A and/or B are polyatomic fragments, current evidence suggests that the energy transfer mechanism is an accurate description. However, in cases where A and B are atoms or simple diatomic molecules (such as OH), both experimental and theoretical evidence has been mounting in recent years that true three-body collisions also contribute significantly. Unfortunately, this evidence has been largely ignored by the chemistry community.

Our objective in this work was to perform quantum mechanical calculations that would add compelling evidence for the existence and importance of true three-body collisions in recombination reactions. It is very important that the correct mechanisms be used in the analysis of kinetics experiments on recombination reactions, or the wrong answers and behavior will be obtained. The issue here is a very fundamental one that affects the whole way one thinks about recombination reactions.

We performed calculations on the reaction,

$$Ne + Ne + H \leftrightarrow Ne_2 + H,$$

which is simple but relevant because it contains all the kinds of states that are involved in any atomic recombination reaction.

The calculations were performed using the vibrational-rotational infinite order sudden approximation, a simple approximate quantum mechanical method that is not valid for most systems but is valid for the Neon atom reaction shown above. This approximation has the advantage that it treats both the three-body and energy transfer mechanisms simultaneously and on exactly the same footing, so that it allows a direct comparison of them. With the vibrational-rotational infinite order sudden approximation, collision cross sections for transitions between all the bound, quasibound, and unbound continuum states of Ne_2 were calculated. Then, detailed rate constants for all these processes were generated from the cross sections, and the master equations governing recombination and collision-induced dissociation in the Ne_2 + H system were accurately solved numerically. These master equations contain all possible processes. Rates allowing only the energy transfer mechanism were also calculated by simply setting the rate constants for the three-body collisions to zero. It was found that, for this reaction, true three-body collisions dominate over the energy transfer mechanism at all pressures. As seen from Figure 1, the energy transfer effective rate coefficient is more than a factor of two too small at low pressures and orders of magnitude too small at high pressures!

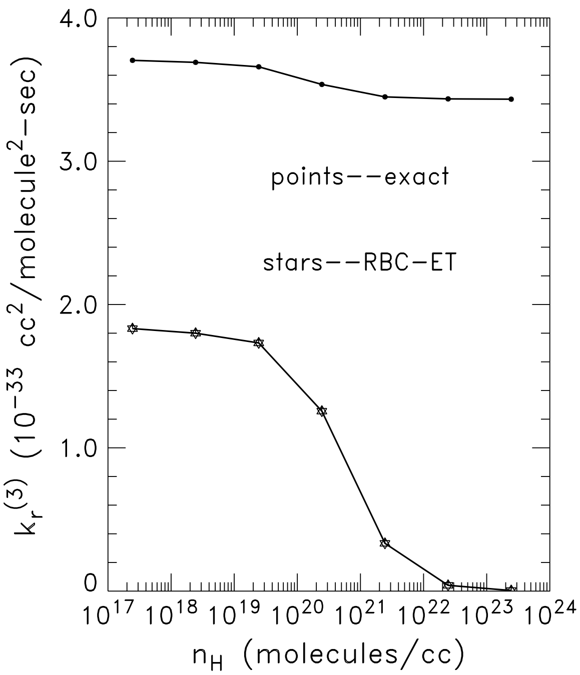

Figure: Semilog plot of the effective third-order recombination rate coefficients at T = 30 K versus third-body number density. The points are for the exact solution of the master equations; the stars are for the energy transfer approximation of Roberts, Bernstein, and Curtiss.

This is the first clear quantum-mechanical evidence of the importance of true three-body collisions in atomic and molecular recombination and collision-induced dissociation reactions. Detailed results of this work as well as a discussion of its implications for general recombination reactions have been published.

This work has attracted a great deal of attention. We have given six invited talks on this topic during its three years of funding. After each talk, several people have responded with comments like, “Wow! That’s totally new to me. I never even thought about three-body collisions!” We have also been asked to give three invited talks on this subject during fiscal year 2000. However, all of these meetings could only pay part of the travel expenses, so we have declined them. With the huge cut in our travel budget, we cannot even attend required DOE meetings much less national and international science conferences.

We are continuing to work along these lines and have almost finished the programming necessary to do exact three-body quantum mechanical calculations to confirm these results. In addition, this research has led to work on recombination in Bose-Einstein condensates of dilute alkali atoms and also has implications regarding the large, anomalous, and unexplained isotope effects seen in the recombination reaction that forms ozone in the atmosphere.

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